



Coupling photo and sono technologies to improve efficiencies in conductive diamond electrochemical oxidation

Fernanda L. Souza^a, Cristina Sáez^b, Pablo Cañizares^b, Artur J. Motheo^a,
Manuel A. Rodrigo^{b,*}

^a Instituto de Química de São Carlos, Universidade de São Paulo, P.O. Box 780, CEP 13560-970, São Carlos, SP, Brazil

^b Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies, Universidad de Castilla – La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

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ABSTRACT

In this work, the improvements obtained in the conductive-diamond electrochemical oxidation (CDEO) by simultaneous coupling of ultrasounds (US) and UV-light irradiation are studied for the treatment of synthetic wastes containing dimethyl phthalate (DMP). Results show that both irradiation technologies improve significantly the rates of oxidation and mineralization of the electrolytic process, but their coupled effect on results is smaller to the effect observed when they operate separately. Results are explained in terms of the formation of radicals in the reaction media by UV-light or US decomposition of powerful oxidants formed electrochemically on the conductive-diamond surface. Oxidation of DMP proceeds through the removal of the methyl esters group, ring breakage and carboxylic acid mineralization. Concentration of intermediates is very small in electrolytes with sulfates. When chlorides are present in the electrolyte, chlorophenols are also observed and concentration of intermediates becomes greater. In terms of energy consumed, sonolysis processes are more expensive than photolysis processes to attain similar removal percentages.

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1. Introduction

During the recent years, many studies have demonstrated that conductive diamond electrochemical oxidation (CDEO) is a very efficient technology for the removal of organic pollutants. The hydroxyl radicals and many other mediated oxidants produced at high concentrations on the surface of diamond are responsible for the harsh oxidation conditions attained. In addition, CDEO exhibits three outstanding properties as compared with other advanced oxidation technologies and with electrolyses with other anodes [1]:

- Robustness, because it is the only process that can assure previously the depletion of the organic load of any waste down to the limit fixed by any regulation.
- Efficiency, because for concentrations over 1500–2000 mg dm⁻³ (depending on the flow conditions of the cell) it uses to show an electric efficiency of 100%. However, its costs depend largely on the organic load of the effluent. In particular, it is very efficient for the coarse treatment of wastewaters polluted with less

than 15–20 g dm⁻³ COD down to the typical discharge limits to municipal sewers.

- Integration capability, because CDEO technology can be easily joined to many other treatment technologies either by using the anodic or the cathodic processes. Some examples of this integration capability are the electro-Fenton and the sono-electrolytic and the photo-electrolytic processes [2].

In spite of the large number of studies done, there is still a long way for its commercial use and many topics remain as hot topics now. Two are of particular interest:

- The specificity of diamond electrodes and the elucidation of the influence of diamond layer characteristics on the efficiency of the oxidation, because a very careful selection of the properties of the electrode surface seems to improve results obtained by CDEO. This is especially important in production of oxidants [3], but it also influences on the treatment of wastes [4]. The improvements which can be obtained by the combination of CDEO with other technologies such as the irradiation of ultrasounds (US) or UV-light, because in the later years light irradiation and/or ultrasounds irradiation have shown to improve results of many advanced oxidation processes, in particular avoiding the production of refractory organics during the oxidation of complex

* Corresponding author. Tel.: +34 902204100x3411; fax: +34 926295256.

E-mail address: manuel.rodrigo@uclm.es (M.A. Rodrigo).

pollutants [5–7]. This is not a problem of the robust CDEO technology, but clarification of how sono- and photo-CDEO can improve results of conventional CDEO is worth of investigation.

Many works have been published during the recent years on photo-electrolysis. Most of them focused on the use of titanium dioxide in thin film or in mixed metal oxides (MMO) anodes [8–18]. They typically study the degradation of dyes, because in addition to their role as pollutants, they consist of large molecules in which synergistic effects of electrochemical and photochemical technologies can be more clearly assessed. However, some works are focused on pharmaceuticals or other complex molecules, with the same aim: assessing the removal of a complex pollutant and, at the same time, use it as a model of large molecule. Results shown in those works indicate that combining photo and electrolysis technologies leads to a synergistic effect explained by heterogeneous (external bias contribute to a decrease in the electron–hole pair recombination process and the UV-photons reaching the electrode surface form excited radicals) and homogenous (photo activation of electrochemically generated reactive species) catalytic processes.

Sono-electrolysis has also been widely studied in the recent years and it has been proposed for the treatment of different types of wastewaters leading to good efficiencies [19–23]. Results shown in those works indicate that ultrasound irradiation is an effective technology to increase mass transport and to produce important changes in the chemical composition of the electrolyte because of the ultrasonic cavitation phenomenon, which takes advantage of the high pressure and temperature produced during the implosive collapse of bubbles irradiated with the ultrasound to form new radical species and components [24,25]. These changes are complementary and even synergistic with those taking place during electrolyses, resulting in very effective processes.

Removal of phthalates, a widely used plasticizer commonly found in urban wastewaters has been studied by sonochemical [26], photochemical [27] and electrochemical methods [28] but, to the authors' knowledge, not a comparative study has been made till now. The goal of this work is to compare the synergistic or antagonist effects of photolysis and sonolysis on the efficiency of the conductive-diamond electrochemical-oxidation of dimethyl phthalate. To do this, CDEO electrolyses, sono-CDEO, photo-CDEO, and sonophoto-CDEO studies are going to be made, and results will be discussed at the light of the influence of the operating conditions on efficiencies and on reaction intermediates formation.

2. Materials and methods

2.1. Chemicals

All chemicals, including DMP (a.r., Sigma–Aldrich), anhydrous sodium sulfate and sodium chloride used as supporting electrolyte (a.r., Fluka, Spain), oxalic acid, maleic acid, tartaric acid, phthalate (a.r., Merck, Spain), hydroquinone, 1,4-benzoquinone, monomethyl phthalate, 4-hydroxyphthalic acid, 4-chlororesorcinol, 2,4,6-trichlorophenol, 2-chlorophenol, 3-chlorophenol, 2,4-dichlorophenol, chlorohydroquinone (a.r., Pan-reac, Spain) were analytical grade and used as received. Acetonitrile HPLC grade (a.r., Sigma–Aldrich, Spain) was used as mobile phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 MΩ cm at 25 °C) was used to prepare all solutions.

2.2. Apparatus and analysis procedures

All samples extracted from electrolyzed solution were filtered with 0.45 μm nylon filters from Whatman before analysis. The concentrations of the compounds were quantified by HPLC (Agilent

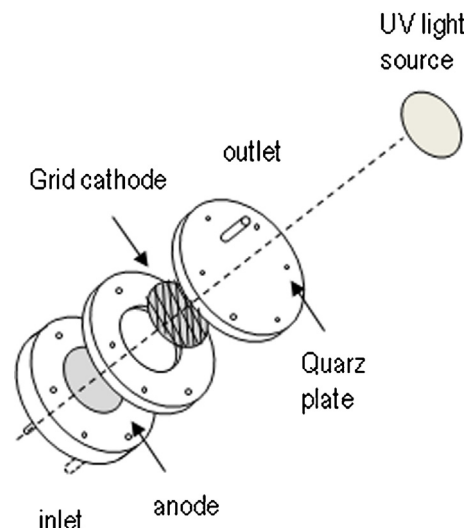


Fig. 1. Scheme of the photo-electrochemical reactor.

1100 series) using analytical column Phenomenex Gemini 5 μm C18. The detection wavelength used was 274 nm and the temperature oven was maintained at 25 °C. Volume injection was set to 50 μL. The mobile phase consisted of 50% acetonitrile and 50% water with a flow rate of 0.3 cm³ min^{−1}. The area of the peak corresponding to the DMP molecule was compared to the one from a calibration curve that was previously obtained in the range of 1–200 mg dm^{−3}. Moreover, the acids intermediates formed during the experiments were detected with a detection wavelength of 190 nm. The ion exchange column used was SUPELCOGELTM H Carbohydrate Columns from Sigma–Aldrich and dilute H₃PO₄ (0.022 M) was employed as the solvent. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Measurements of pH were carried out with an InoLab WTW pH-meter. The chemical oxygen demand (COD) was monitored using a HACH DR200 analyzer. The samples containing chloride concentration up to 2 g dm^{−3} were diluted as recommended.

2.3. Electrochemical cell

Electrolyses were carried out in a single compartment electrochemical flow cell. One of the covers of this cell was made of quartz in order UV light to access into the reaction media. The other cover was made of a high chemical resistance polymer. The anode was pasted to the polymer cover and a grid cathode to the quartz cover in order to let light irradiates the cathode, anode surface and the interelectrode gap (Fig. 1). Conductive–diamond electrodes (p-Si–boron-doped diamond) were used as anode and a grid of stainless steel as cathode. Both electrodes were circular (100 mm diameter) covering a geometric area of 78 cm². The interelectrode gap was about 9 mm. A UV lamp VL-215MC (Vilber Lourmat), λ = 254 nm, intensity of 930 μW/cm² and energy 4.43–6.20 eV irradiating 15 W directly to the quartz cover. The ultrasound generator was a UP200S (Hielscher Ultrasonics GmbH, Germany) equipped with a titanium glass horn of 40 mm diameter, length 100 mm, emitting 24 kHz and maximum ultrasonic power 200 W. The output can be continuous or pulsed with varying percentage of cycle duty ranging from 10 to 100%.

Boron-doped diamond films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si <100> wafers (0.1 Ω cm, Siltronix). Prior to use in galvanostatic electrolysis assays, the electrode was

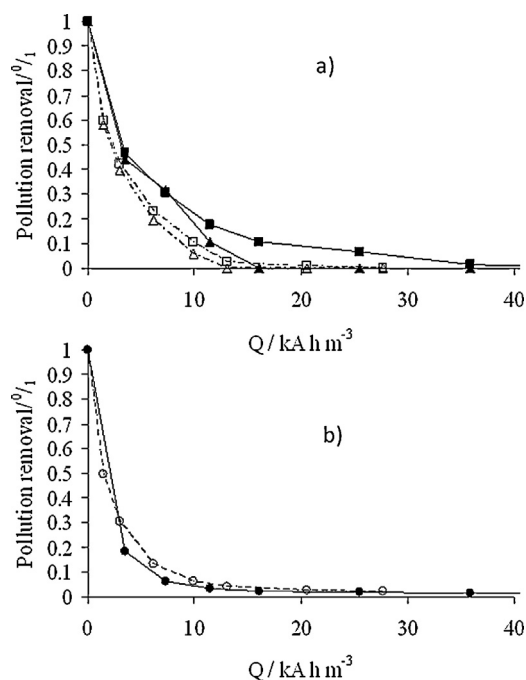


Fig. 2. Removal of pollutants during the electrolysis (●, DMP; ■, COD; ▲, TOC) and sonophoto-electrolysis (○, DMP; □, COD; △, TOC) with conductive-diamond anodes of DMP solutions in at 20 mA cm^{-2} .

polarized during 10 min in a $1 \text{ M Na}_2\text{SO}_4$ solution at 15 mA cm^{-2} to remove any impurities from its surface.

The cell reactor was connected to a peristaltic pump (flow rate $26.4 \text{ dm}^3 \text{ h}^{-1}$) to a reservoir through silicon tubes. A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point (25°C).

The electrooxidation was carried out galvanostatically using 0.80 dm^3 of a solution containing 161.8 mg dm^{-3} DMP, which corresponds to an organic carbon content equal to 100 mg dm^{-3} . The investigated variables in the electrochemical degradation of the DMP compound were: (i) the nature of the support electrolyte (NaCl and Na_2SO_4) by keeping the ionic strength at 0.15 mol dm^{-3} , (ii) the applied current density (20 – 120 mA cm^{-2}) and (iii) concentration initial of DMP. All the experiments were carried out at 25°C . The cell voltage did not vary during the electrolysis experiments, indicating that conductive-diamond layers did not undergo appreciable deterioration or passivation phenomena.

3. Results and discussion

Fig. 2 compares changes in the DMP concentration, COD and TOC during the treatment of a synthetic waste containing DMP and sodium sulfate as electrolyte by CDEO electrolysis and sonophoto-CDEO.

As it can be observed, the three parameters are completely depleted during the treatment with both technologies, indicating that both technologies are effective in the degradation of this plasticizer. In addition, a clear improvement is obtained with the use of ultrasounds and UV light irradiation, in terms of a smaller requirement of electric charge for the depletion of the organics. This improvement is clearly observed for COD removal and mineralization (TOC removal) but not for the removal of DMP in which the single electrolytic process (no irradiation of light and ultrasounds) seems to attain a better performance. This clearly indicates that irradiation of ultrasounds or light help to the progress of hard oxidation processes, but it is not very effective in the more single

oxidation of functional groups required to transform DMP in intermediates. Anyhow, the goal of a waste treatment is not the depletion of DMP but the mineralization of the waste and, consequently, light and ultrasounds irradiation exhibits a clear good effect.

Another important observation is the occurrence of a significantly high value of COD when TOC is completely depleted. Not a clear explanation was found for it, although two possibilities could explain the results obtained:

- the accuracy of the analytical techniques or
- the production of hydrogen peroxide that, in spite of being a well-known oxidant, produces COD as a consequence of being oxidized to oxygen by COD reagents. This later process should not be very important because of the well-known low production with stainless steel cathodes

The important improvement found with UV and light irradiation has to be explained in terms of the effect expected for both processes on the electrolytic treatment. Thus, it is known that in a conductive-diamond electrochemical-oxidation process, hydroxyl radicals play a very important role in the mechanism of the oxidation and on the efficiency of the process. This radical is formed by water oxidation on the surface of the diamond electrode (Eq. (1)) and due to its very short lifetime its action is limited to the nearness of the electrode surface. This explains that single CDEO processes behave similarly to direct electrolysis processes, because mass transport is usually limiting the kinetics of the process.



In addition to hydroxyl radicals, it is known that many oxidants are produced on the electrode surface. These oxidants are known to extend the oxidation of pollutants from the nearness of the electrode surface toward the bulk of the wastewater. In the case of sulfate, it is well-known [29] the production of peroxosulfates on the anode, and it is also reported the formation of ozone and hydrogen peroxide [30]. These reagents are typically found in the electrolyte during the electrolysis of wastewaters with CDEO and they are formed according to Eqs. (2)–(5).



Light irradiation is known to promote the production of sulfate radical from persulfate as it is shown in Eq. (6) [31,32]. It is worth taking into account that the sulfate radical reacts typically 10^3 – 10^5 times faster than the anion persulfate [33].



In addition, other oxidants are decomposed by UV light (Eqs. (7) and (8)), helping to explain the better results obtained by photoirradiation because of the activation of oxidants produced electrochemically [15].



Opposite to single electrolytic process the effect of these radicals can be extended to the bulk in a photoelectrolytic process, because in spite of their short lifetime, they are produced not on the surface but in the bulk by decomposition of more stable oxidants.

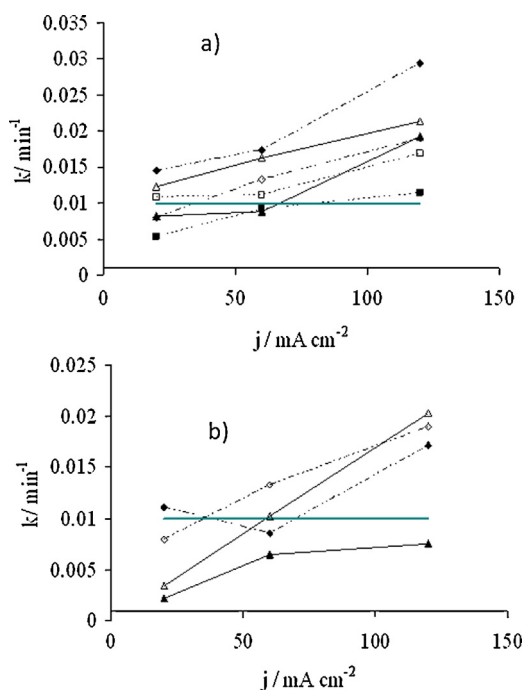


Fig. 3. Influence of the current density on the oxidation rate of DMP by electrolyses (◆, DMP; ■, COD; ▲, TOC) and sonophoto-electrolyses (◇, DMP; □, COD; △, TOC) in (a) sulfate media and (b) chloride media.

Production of radicals by sono-processes is based on a different mechanism. US irradiation produces huge concentrations of energy in very small places (hot spots), resulting in a local temperature of several thousands of Kelvin [4]. This energy is dispersed to the surroundings so that the gas temperature in the hot spot quickly returns to the ambient value. However, during a very short time it can produce significant changes in chemical composition and can form new radical species and components in the system. Hence, in a reaction media like the one used in this study, it is expected the formation of sulfate and hydroxyl radicals due to this process. These radicals are not necessarily produced on the surface of the electrode but in the bulk, improving the efficiency of the process.

Coming back to Fig. 2, as it can be seen, charge course of experimental pollution decay is exponential and so it is the time course, because the experiments were done in galvanostatic conditions (at constant current density). This means that pollutant decay can be properly modeled with a first order kinetic, which in electrochemical oxidation processes stands for processes whose rate is controlled by mass transport or for mediated electro-oxidation. As shown in Eqs. (9) and (10), both kinetic can be modeled as first order expression if:

- concentration of pollutant is considered to be nil on the surface of the electrode (proper assumption in the case of mass transport) and

$$r_{\text{mass_transport}} = K_L A (C_{\text{pollutant}} - C_{\text{pollutant_surface}}) \approx k C_{\text{bulk}} \quad (9)$$

- concentration of oxidants which produces mediated processes is considered to be constant (pseudo-steady state approach)

$$r_{\text{mediated_oxidation}} = K_{\text{ox}} \cdot C_{\text{ox}} \cdot C_{\text{pollutant}} \approx k C_{\text{pollutant}} \quad (10)$$

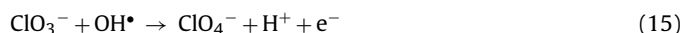
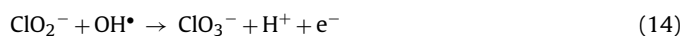
Fig. 3 shows the kinetic constants obtained after fitting the experimental degradation results to a model. This model consists of a single mass balance with a first order kinetic. As states before, this model reproduces well the decay of every parameter during the CDEO and sonophoto-CDEO of DMP in sulfate media. It was

also observed to be successful in the description of the processes in chloride-containing supporting electrolyte.

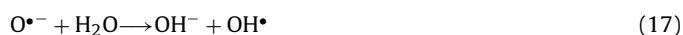
As it can be observed, rates in sulfate media are higher than those fitted in chloride media. Current density has a positive effect on the kinetic constant, although it is not always linear, suggesting the contribution of many processes. Irradiation of light and ultrasound always improves the mineralization and the oxidation progress although this does not happen with DMP which exhibits a worse behavior in the irradiated electrolyses in sulfate media but not in chloride media. Rates of COD removal in chloride media were not calculated because of the strange behavior of this parameter which was depleted very rapidly (even when significant amounts of DMP and TOC are still present in the reaction media) indicating some sort of analytical problem with this measurement. Main difference between the treatment of wastes containing sulfates or chlorides come from the different radicals and oxidants formed. Electrolysis of chloride with many electrodes lead to the formation of hypochlorite as the main final product and both, the direct and the mediated oxidation mechanisms have been demonstrated (Eqs. (11) and (12)).



However in the case of using conductive-diamond anodes, the improved action of hydroxyl radical promotes the oxidation of hypochlorite to other species, such as chlorite, chlorate and perchlorate (Eqs. (13)–(15)), being perchlorate the final product in the oxidation [34–36].



This explains that oxidation of organics in the presence of chlorine is not a very effective process with diamond anodes as compared with other anodes such as those containing mixed metal oxides (MMO anodes). Light irradiation effect on electrolysis should be focused on the decomposition of hypochlorite. This reaction has been studied in the literature [37,38], and it has been demonstrated that under non extreme pH, hydroxyl and chlorine radicals are the main products resulting of the light assisted degradation of hypochlorite (Eqs. (16) and (17)).



The production of these oxidants in the bulk, help to explain the better results obtained by sonophoto-CDEO. However, the poorer results (as compared with those obtained in the sonophoto-CDEO in supporting electrolytes with sulfates) clearly indicate that sulfate radicals are playing a very important role in this processes, even more important than that of chlorine or hydroxyl radicals.

Fig. 4 shows the maximum concentration observed for the main intermediates monitored by HPLC in the treatments of wastewaters containing sulfates as electrolyte. Oxidation attained in both processes is very harsh and significance of intermediates is small. Main aromatic intermediates are monomethyl phthalate, phthalic acid and 4-hydroxyphthalic acid and the main non-aromatic intermediates are maleic acid and especially oxalic acid. Although small, the concentrations of this latter compound were found to increase at large current densities and with light and US irradiation, opposite to what it could be expected according to the effect of both technologies in other AOP (promoting the depletion of intermediates).

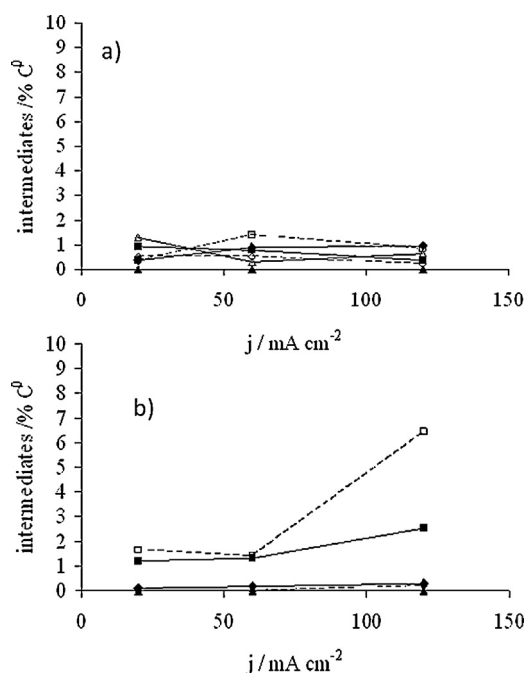


Fig. 4. Maximum concentrations of intermediates found during the electrolyses (full points) and sonophoto-electrolyses (empty points) of dimethyl phthalate in sulfate media. (a) \blacklozenge and \diamond : monomethyl-phthalate; \blacksquare and \square : phthalic acid; \blacktriangle and \triangle : 4-hydroxyphthalic acid. (b) \blacklozenge and \diamond : maleic acid; \blacksquare and \square : oxalic acid; \blacktriangle and \triangle : tartaric acid.

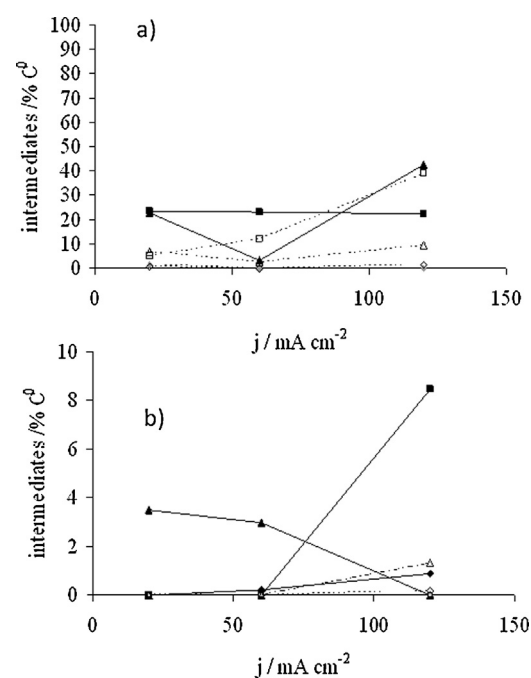


Fig. 5. Maximum concentrations of intermediates found during the electrolyses (full points) and sonophoto-electrolyses (empty points) of dimethyl phthalate in chloride media. (a) \blacklozenge and \diamond : monomethyl-phthalate; \blacksquare and \square : phthalic acid; \blacktriangle and \triangle : chlorophenols. (b) \blacklozenge and \diamond : maleic acid; \blacksquare and \square : oxalic acid; \blacktriangle and \triangle : tartaric acid.

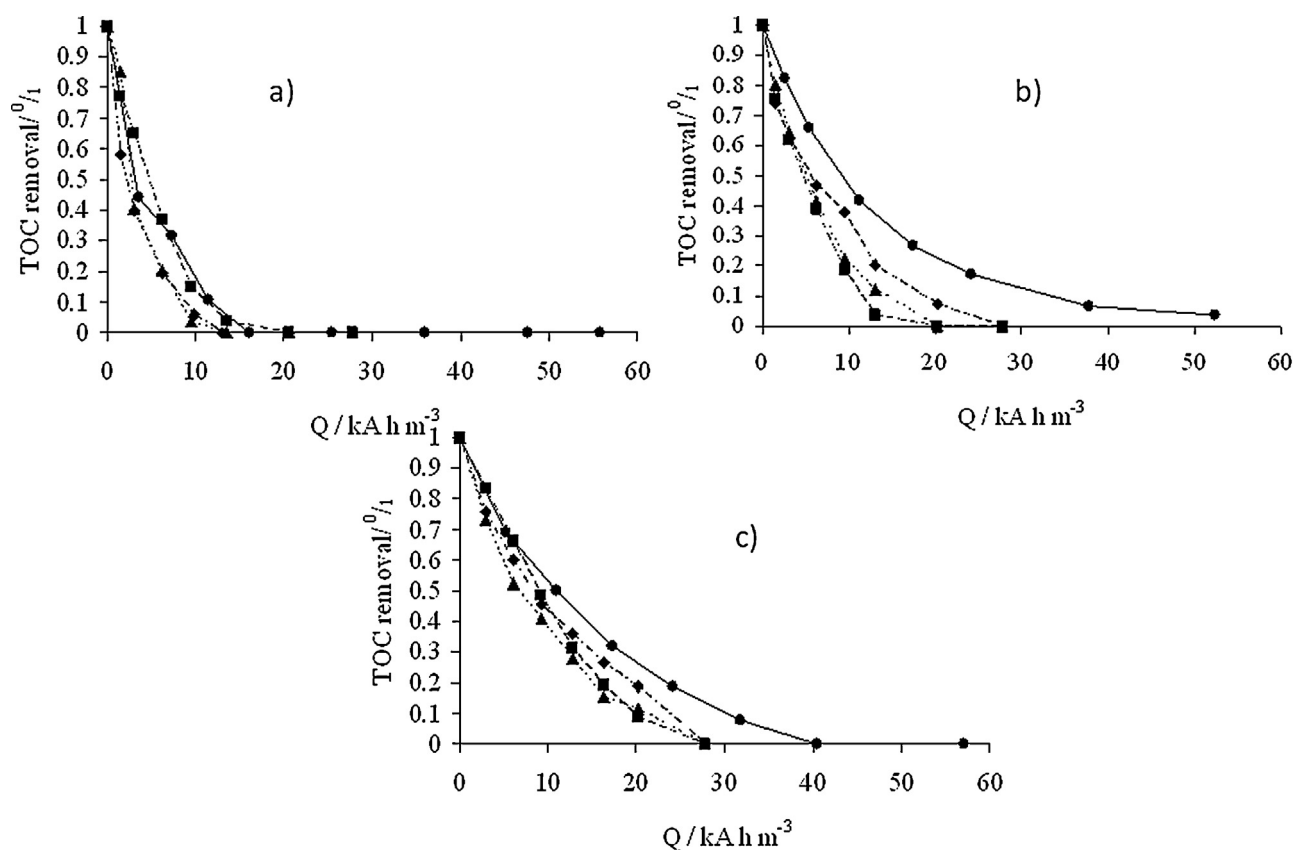


Fig. 6. Removal of TOC during electrolysis (●), sono-electrolysis (■), photo-electrolysis (▲) and sonophoto-electrolysis (◆) with conductive-diamond anodes of DMP solutions sulfate medium. (a) 20 mA cm⁻²; (b) 60 mA cm⁻²; (c) 120 mA cm⁻².

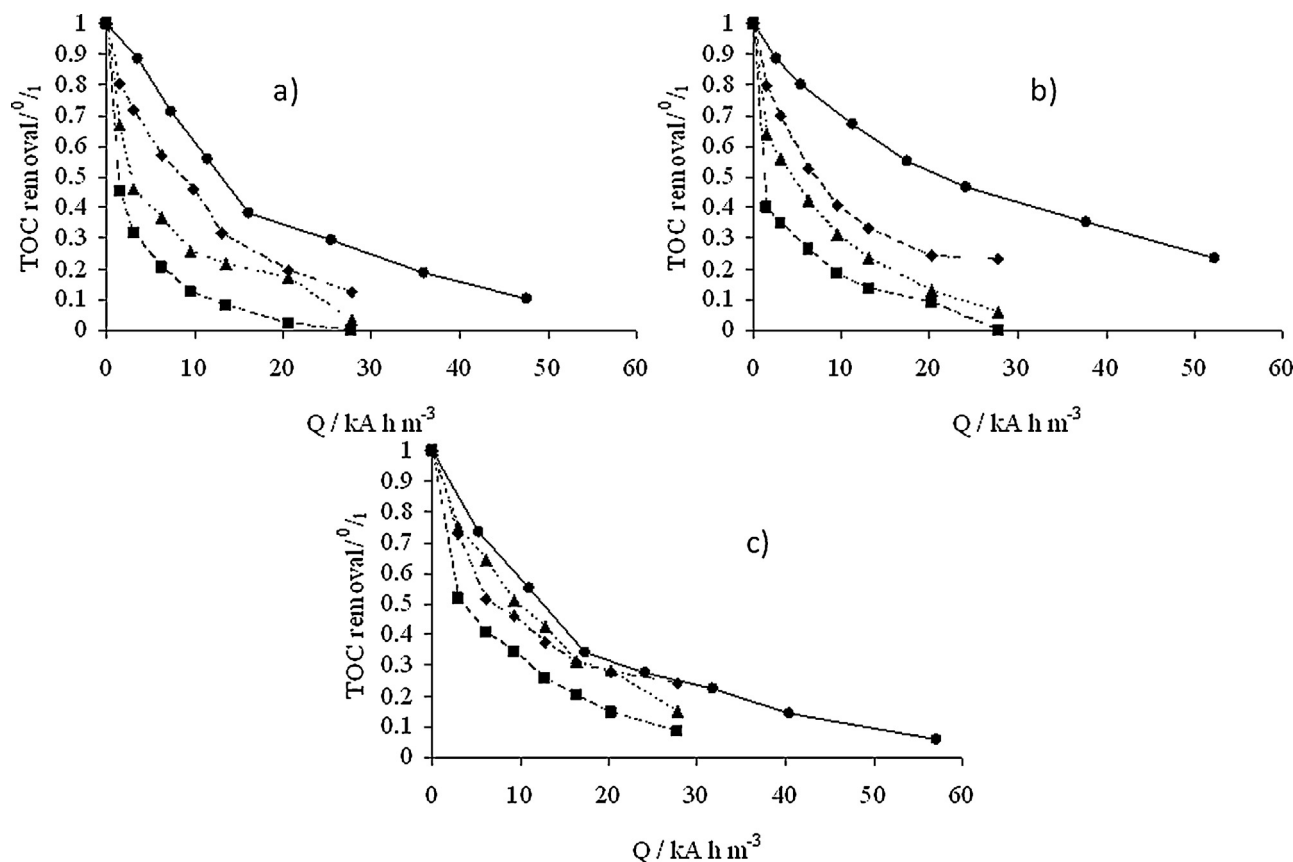


Fig. 7. Removal of TOC during the electrolysis (●), sono-electrolysis (■), photo-electrolysis (▲) and sonophoto-electrolysis (◆) with conductive-diamond anodes of DMP solutions in chloride medium. (a) 20 mA cm⁻²; (b) 60 mA cm⁻²; (c) 120 mA cm⁻².

It is important to remind that, in every case, these species behave as intermediates and that complete mineralization of the synthetic wastewaters was obtained.

Presence of intermediates in terms of concentration is more important when chlorides are contained in the supporting electrolyte, because of the very significant role of chlorine and hypochlorite on the oxidation. This can be clearly observed in Fig. 5, in which it is important to remark that concentration of phthalate increases by one fold. In addition, two new species appear as intermediates: chlorophenols and tartaric acid. No chlorinated carboxylic acids were detected during the electrolyses (at least in concentrations which could be detected by HPLC). This is a surprising result because in previous studies of our group about the treatment of chlorophenols [39,40] the chlorinated carboxylic acid seemed to play a significant role in the oxidative destruction of chlorophenols. In chloride media, the irradiation of ultrasounds and light seems to have a harsh effect on non-aromatic intermediates, because the concentration of oxalic acids was almost nil and just small concentration of tartaric acid was detected at large current densities.

Results have clearly shown that US and UV irradiation improve the performance of CDEO processes in the removal of pollution. However, it is important to study the separated effect of both irradiation technologies. To do this, Fig. 6 compares the effect of ultrasounds and light irradiation on the mineralization attained during the electrolyses of synthetic wastes containing sulfates as supporting electrolyte in four different cases. Electrolysis with diamond electrodes is very effective and they are always capable of removing DMP within the range of current densities studied. As expected in electrolytic wastewater treatment processes, the process efficiency is higher at lower current densities, although it has

to be taken in mind that the process rate is also lower at these conditions. Irradiation of ultrasounds or light has a positive effect on results leading to lower electric charges for the complete mineralization of the waste. However, opposite to what can be expected, there is not a synergistic but a clear antagonistic effect on results, with the simultaneous irradiation of light and ultrasounds.

This effect should be explained in terms of an excessive formation of radicals which instead of attacking DMP (or reaction intermediates) combine among them to form more stable and less aggressive oxidants which have a smaller oxidation capability and can decompose forming oxygen. Eqs. (4) and (18)–(20) summarize some of the reactions that could explain this behavior in our experimental system.



The same observations are applicable to electrolyses of synthetic wastes containing chlorides instead of sulfates as supporting electrolyte, although in this case the effect of every parameter is even clearer because curves are more separated, as it can be observed in Fig. 7. Electrolytic treatment with irradiation of ultrasounds clearly overcomes the other treatments. In addition, comparing both supporting electrolytes, it seems clear that mineralization is more efficient in sulfate media than in chloride media. This can be easily explained by the more drastic oxidation of persulfates than that done by chlorine reagents and by the important role suggested below for the sulfate radicals.

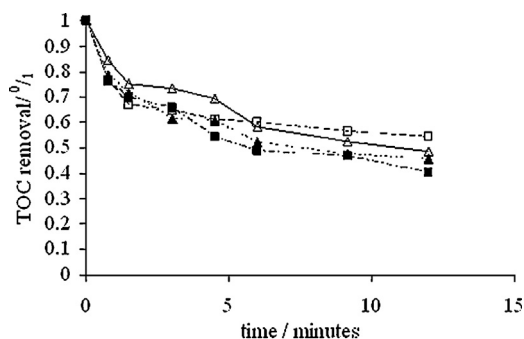


Fig. 8. Removal of TOC during the sonolyses and photolysis of DMP solutions of chloride or sulfate medium. ■: photolysis in chloride media; ▲: photolysis in sulfate media; □: sonolysis in chloride media; △: sonolysis in sulfate media.

Finally, a point that should be clarified is the performance of the single sono and photo irradiation. Fig. 8 shows mineralization attained by single sonolysis and single photolysis technologies in both chloride and sulfate aqueous electrolytes. As it can be observed, opposite to electrolytic technologies, supporting electrolyte does not influence on results in both technologies. This confirms that differences observed in the electrolytic processes can be explained because of the decomposition by US or UV irradiation of more stable oxidants formed on the electrode surface. In addition, photolysis is much more efficient than sonolysis because it attains a faster removal even with the irradiation of 10 times less energy (UV 37.5 W dm^{-3} irradiation power vs. 500 W dm^{-3} US irradiation power). For comparison purposes, power supplied in the electrolytic treatments done in this work ranges between 15 and 240 W dm^{-3} for current densities ranging between 20 and 120 mA cm^{-2} , respectively. This means that coupled processes, in particular photo-CDEO can be very promising from the view point of minimization of operation costs.

4. Conclusions

From this work, the following conclusions can be drawn:

- Dimethyl phthalate can be successfully oxidized using conductive-diamond electrochemical oxidation. Light and ultrasound irradiation improves very importantly the efficiency of the electrochemical process in an integrated sonophoto-electrochemical process.
- The improvement attained in the CDEO with the application of both irradiation technologies is smaller to that of the application of them separately, indicating that the combination of the two technologies with the electrochemical process show a clear antagonistic effect.
- In single irradiation processes there are no differences caused by the electrolyte composition (in particular presence of sulfate or chlorides). Improvements in the electrolytic treatment attained with irradiation of UV-light and US can be explained by the formation of radicals by decomposition in the bulk of the oxidants formed on the surface of the electrode.
- Both the CDEO and the sonophoto-CDEO produce the same intermediates. Main aromatic intermediates are monomethylphthalate, phthalic acid and 4-hydroxyphthalic acid. Main non-aromatic intermediates are maleic acid and especially oxalic acid. These intermediates are found in combined and single processes and also reported in literature for other AOP, indicating that oxidation of DMP proceed through the removal of the methyl esters group and the breakage of the aromatic ring to form carboxylic acids that are finally mineralized to carbon dioxide. In the presence of chloride, production of chlorophenols

and tartaric acid and increases in the concentration of all intermediates are the main differences observed.

- US irradiation is less efficient in terms of energy requirements than UV-irradiation and CDEO.

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